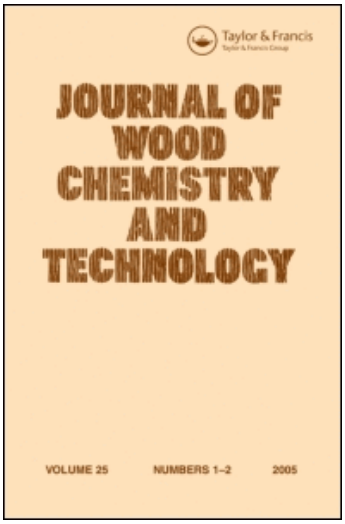

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The Influence of Anthrahydroquinone and Other Additives on the Condensation Reactions of Vanillyl Alcohol

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THE INFLUENCE OF ANTHRAHYDROQUINONE AND OTHER ADDITIVES ON THE CONDENSATION REACTIONS OF VANILLYL ALCOHOL

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ABSTRACT

Vanillyl alcohol, a simple lignin model, has been heated with alkali under a variety of conditions and in the presence of several additives. The level of condensed products, principally dimers and trimers, has been determined in each case. Some additives, such as sulfide and anthraquinone, showed few differences from the control. Other additives, such as anthrahydroquinone, dithionite and 3,5-dinitrobenzoic acid, greatly depressed the levels of condensation products. The detection of a minor product, a head-to-head dimer, suggests some radical intermediates are present under these reaction conditions. The degree of condensation and ratio of products was quite temperature dependent. The influence of selected additives on the condensation reactions of a dioxane lignin has also been studied.

INTRODUCTION

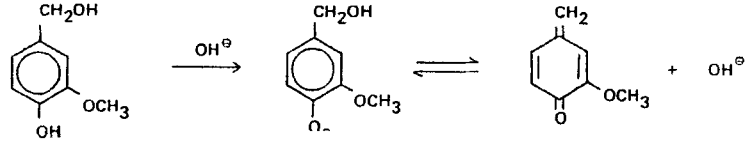
The delignification of wood can be thought of as involving two primary reactions: first, a set of fragmentation reactions in which high molecular weight lignin is degraded into smaller units, some of which are water soluble and pass from the wood cellular structure to the cooking liquors, and second, condensation reactions in which lignin and/or lignin fragments combine to form high molecular weight material containing new types of bonds.[1,2] This latter process is an undesirable one in that the condensed lignin is probably more resistant than the native lignin to solubilization and may contribute to "residual" lignin (that lignin which is the most difficult to remove during pulping).[2]

One of the principal benefits of employing catalytic amounts of anthraquinone (AQ) during alkaline pulping is rapid delignification rates.[3] Anthrahydroquinone (AHQ), which is formed during pulping by the reaction of AQ with wood carbohydrates,[4-6] has been shown by a number of research groups to promote fragmentation reactions of lignin model compounds.[7-10] We would like to describe here our efforts to show that AHQ can also inhibit condensation reactions in a simple lignin model, namely vanillyl alcohol. The significance of this finding is that it predicts that pulping to low residual lignin contents should be possible in the presence of AQ; this has recently been realized in our laboratory.[11]

RESULTS AND DISCUSSION

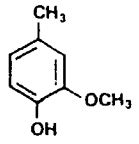
Vanillyl Alcohol Cooks

The condensation reactions of actual lignin would be expected to generate a very complicated product mixture. In an attempt to understand the chemistry of the process at a molecular level, we chose to study a model, vanillyl alcohol (1), which has some of the essential features of typical lignin. In hot alkali, 1, in its phenoxide form (2), should reversibly form a quinonemethide (3), equation 1. Many of the reactions of lignin, including condensation reactions, are postulated to proceed through quinonemethide intermediates.[1,2]



1 2 3

If AQ or AHQ were to favorably interfere with vanillyl alcohol (VA) condensation reactions, one might observe (a) less polymer formation in the presence of the additives, relative to a control, (b) reduction products, such as creosol (4), and/or (c) oxidation products, such as vanillin (5) and vanillic acid (6).



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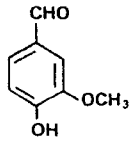

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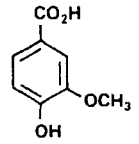

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Dilute solutions of vanillyl alcohol in 0.5N NaOH, containing no additives (the control), equal molar amounts of AQ, 3 molar equivalents of glucose or combinations thereof, were heated at 173° (a typical pulping temperature) for 2 hours, under mild agitation, in sealed titanium reactors. The purpose of the glucose was to reduce AQ to AHQ. Since glucose is rapidly destroyed by base at elevated temperatures,[12] there may not be a continuous generation of AHQ from AQ during the course of the cook. Consequently, equal molar amounts, rather than catalytic levels, of AQ were generally used. The products were worked-up by either (a) freezing-drying the acidified mixture or (b) filtering to remove AQ, acidifying and collecting the organic precipitate.

Analysis of the underivatized products by high pressure gel permeation chromatography (GPC) was not successful. Columns which were capable of differentiating small polymers, i.e., combinations of μ-Bondagel and μ-Porasil, did not function properly with the solvents necessary to dissolve the products. The SynCrompak column used in earlier studies[13] showed very few differences between product samples; this column is not able to distinguish molecular weight differences below 5000. Consequently, GPC analysis did not allow a distinction to be made as to the degree of polymerization in the control runs vs. the runs containing additives.

Direct gas chromatographic (GC) analysis of precipitated and freeze-dried products showed very few signals; creosol, the expected reduction product of quinonemethide 3, was not observed. Product samples which were extracted with hot tetrahydrofuran (THF), derivatized by methylation with dimethyl sulfate to increase the volatility of phenolic components and then analyzed

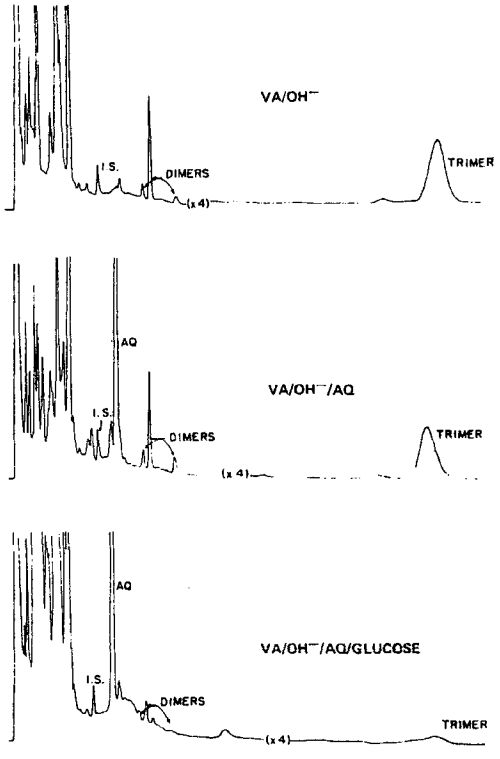


Figure 1. Reproductions of the Gas Chromatograms Obtained from Derivatized Products of Three Vanillyl Alcohol (VA) Cooks

by GC showed many more signals. Figure 1 shows the gas chromatograms of three cooked samples, containing the same amount of added internal standard (I.S.).

The cooked sample which contained AHQ (actually AQ and glucose) showed substantially lower amounts of dimers and trimers. (Proof of these structures will follow.) The chromatograms of the control sample and the one containing only AQ as an additive had nearly identical levels of dimers and trimers (Fig. 1, top two). Approximate yields of 4 and 5% were calculated for the main dimer and trimer, respectively, in the control and AQ cooks by assuming

a GC response factor of 1.0 for these materials relative to the internal standard. When only glucose was used as an additive (GC curve is not shown in Fig. 1), the yield of main dimer and trimer was 3 and 1.3%, respectively. For the glucose/AQ additive mixture the yields were 1.5 and < 0.5% for the dimer and trimer.

The GC analyses of derivatized precipitated products were similar to those of the freeze-dried products, showing the same trends as just discussed. Glucose, alone, as an additive to the vanillyl alcohol cooks caused some decrease in levels of dimers and trimers, but not nearly to the extent of the glucose-AQ (i.e., AHQ) combination. One can speculate that glucose or its by-products might capture quinonemethides in irreversible reactions, thereby lowering the concentration of quinonemethide (QM) species and interfering with condensation reactions. Possibly AHQ can behave in a manner similar to glucose.

Analyses of the ether soluble portion of precipitated cooked samples by proton nuclear magnetic resonance (^{1}H-NMR) also showed that the control and AQ runs gave similar products, but the AHQ run produced additional aromatic signals in the 7.3-7.6 δ region and a sharp signal at 4.3 δ. Because of the method of workup, i.e., prolonged air exposure and filtration, the new signals in the aromatic region cannot be attributed to AHQ. Condensation reactions should produce $ArCH_2$-Ar units, which will appear around 3.7-4.0 δ.[14] This same region also contains $ArOCH_3$ signals. The aromatic signals for phenols and aromatic ethers occur in the 6.5-7.1 δ region of the spectrum. In comparing the spectra of the cooked samples, one can see that the AHQ sample has less relative intensity in the $OCH_3/ArCH_2Ar$ region than the other samples. This is another indication that less condensation reactions have occurred in the presence of AHQ.

What is the cause of the signals in the 7.3-7.6 δ region which are so strong in the AHQ system and so weak in the others? This region is characterized by unsubstituted aromatics or aromatics which have no strong electron withdrawing or releasing substituents. Consequently, in our case this region would have to

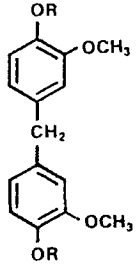
represent a vanillyl alcohol stripped of its aromatic oxygens (quite unlikely) or an AQ type molecule in which one or both carbonyl groups have been modified.

Product Characterization

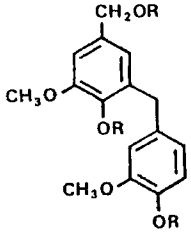
The general method of characterization of the vanillyl alcohol condensation products was by gas chromatography - mass spectroscopy (GC/MS), although the major dimer and trimer were also collected by preparative GC and NMR spectra were recorded. The full details of the mass spectral interpretation of the fragmentation patterns of condensed products is reported in the next paper.[15]

The three most prominent components directly following AQ in the gas chromatogram (Fig. 1) showed mass spectral molecular ions of 288, 288 and 332, which would correspond to methylated dimers of vanillyl alcohol (molecular weight 154). The molecular ions were quite intense, which is indicative of highly aromatic structures.

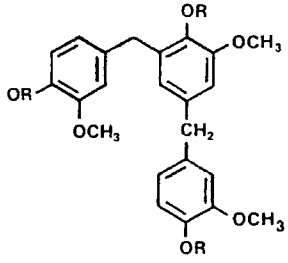
Based on the fact that a dimer of structure 7 had been previously isolated from a vanillyl alcohol alkali reaction[16] and its molecular weight after methylation would be 288, we assumed that one of the dimers corresponded to structure 8. Compound 7 was synthesized[17] and methylated; the resulting product was identical to the most abundant dimer in GC retention time, mass spectrum and NMR. The structure of the other mass 288 dimer is unknown at this time. The third dimer component probably corresponds to structure



7, R = H
8, R = Me



9, R = H
10, R = Me



11, R = H
12, R = Me

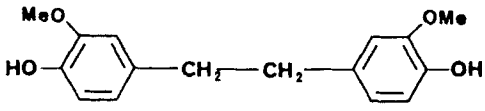
9, since methylation of 9 would give a species of molecular weight 332, 10.

The long retention time component, referred to in Fig. 1 as a trimer, was assumed to be structure 12, based on a mass spectrum displaying an intense molecular ion at 438 and fragment ions at m/e 287 and 151 and on a NMR spectrum that possessed the proper chemical shifts and ratio of aliphatic to aryl protons.

During the course of our investigation, both Yoon, et al.,[18] and Hemmingson and Leary[19] have reported on the self-condensation reactions of vanillyl alcohol. These workers isolated dimer - pentamers by exhaustive column chromatography. The structures of the condensed products, principally as their acetate derivatives, were characterized by spectral means and elemental analyses. Dimers 7 and 9 and trimer 11 have been characterized by both of these groups and their data agree well with our own.

Yoon and coworkers[18] report higher yields than we observed; this may be related to (a) assumptions made by us with regard to GC response factors and (b) differences in reaction temperatures - we worked at much higher temperatures. Temperature does have a dramatic effect. Heating vanillyl alcohol at 60° in alkali changed the ratio of dimers; under these conditions, 9 was the most abundant isomer. Possible mechanisms for the formation of dimer 7 and trimer 11 are shown in Fig. 2.

Other components which we have detected and characterized as part of the vanillyl alcohol condensation products are: methyl ethers of vanillyl alcohol, vanillin, dimer 13, QM-AHQ adduct 14[13]



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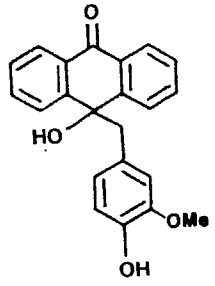

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PROBABLE MECHANISMS OF FORMATION AND STRUCTURES FOR THE MAJOR VANILLYL ALCOHOL CONDENSATION PRODUCTS

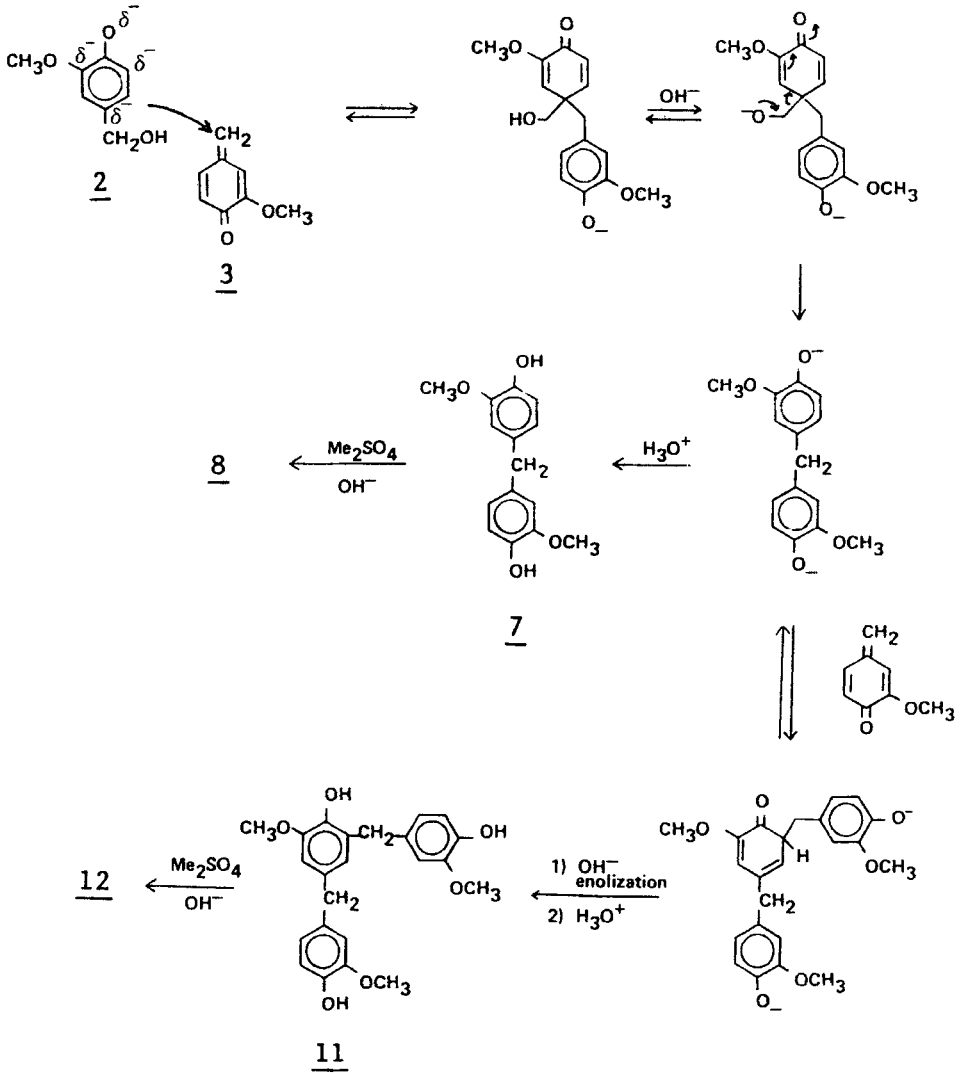


Figure 2. Possible Mechanisms of Formation for the Major Vanillyl Alcohol Condensation Products

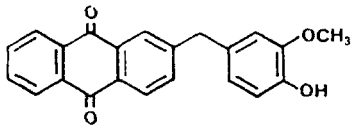
and AQ. Authentic samples of each of these were either purchased or synthesized and were shown to have identical GC retention times and mass spectra to those found in the condensation product mixture. With reference to Fig. 1C, the adduct corresponds to the small signal between the dimer/trimer region, dimer 13 is a very small signal in the dimer region (better seen in subsequent chromatograms) and VA and vanillin are part of the low retention time components.

The adduct 14 was peculiar to the AHQ cook; the others mentioned above were present in all the cooks. Except for the adduct, there were no products which gave clues as how AHQ was retarding condensation reactions. Vanillin, for example, was no more abundant in the additive runs than in the control. Reduction product creosol and oxidation product vanillic acid were not observed in the AHQ runs, even though extraction procedures were employed specifically to look for them. Reduction products of AQ, such as anthracene, which could account for the 7.3-7.6 δ NMR signals noted earlier, were not observed. The low retention time regions of the gas chromatograms were thoroughly examined by GC/MS for minor components such as these.

The formation of dimer 13 suggests there is some radical character to the condensation process, since ionic intermediates would not be expected to couple in a head-to-head fashion.

Several unusual dimer and trimer products have been observed by GC-MS using chromatography conditions different from that shown in Fig. 1. For example, the GC-MS data suggest[15] structures which are isomers of 9 and 11 that possess biaryl linkages meta, rather than ortho, to the phenolic hydroxyl groups. It is difficult to imagine a simple carbanion process (as shown in Fig. 2) that will explain these products. Acidic self-condensation reactions of vanillyl alcohol have been reported to give these unusual products;[19] perhaps they can form to some extent in our case during the mildly acidic workup of the VA cook samples.

Another compound which was expected to be a component of the VA condensation product mixture was 2-vanillylanthraquinone (15).



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This compound has been isolated in low yield from pulping liquors.[20] The VA/AHQ cook sample produced a weak spot on a thin layer chromatography plate displaying the same R_f value and fluoroscent quenching characteristic as 15. The compound was not specifically observed by GC/MS.

Variations in the Cooking Procedures

In the vanillyl alcohol reactions described so far, we used equal molar amounts of AQ (or AHQ) and vanillyl alcohol. What would happen if low levels of AHQ were used? To answer this question we repeated the vanillyl alcohol cooks at various levels of AQ in the presence of excess glucose (Table 1). Most of the decrease in dimer and trimer levels occurred with just a 2.5% level of AHQ; larger amounts of AHQ, however, led to decreased levels of condensation products and increased levels of adduct. Another trend was that the level of trimer appeared to fall off more rapidly than the dimer. Presumably, this is a consequence of having consecutive reactions.

The control cook in Table 1 (AHQ = 0%) gave somewhat different levels and ratios of dimers to trimer than that reported earlier (Fig. 1). Numerous comparisons of VA *vs*. VA/AQ glucose cooks at 173° have been performed and, although the absolute values of constituent levels varied somewhat, the additive runs always had significantly lower levels of dimers and trimer. In comparing additive effects, the cooks were done simultaneously; for example, the data of Table 1 were generated under identical conditions (the mixing oil bath apparatus has space for seven pressure vessels).

The dramatic effect of low levels of AHQ on the VA condensation reaction suggests a (redox) catalytic action. The question

TABLE 1

Vanillyl Alcohol Cooks[a]

% AHQ[bc]	Relative Levels of Products[d]		
	Dimer	Trimer	Adduct
0.0[e]	3.5	8.5	--
2.5	1.4	1.3	0.2
5.0	1.3	0.9	0.5
10.0	1.2	0.7	0.2
20.0	1.1	0.4	0.7
40.0	1.1	0.2	0.8
100.0	1.0	0.2	0.7

[a]Two hours at 173°C, 30 mL of 0.5N NaOH, 154.0 ± 0.6 mg of vanillyl alcohol, titanium bombs, flushed with N_2 before sealing.
[b]Generated by adding the appropriate weight of AQ to the reaction mixture containing 540 mg of glucose. The percent is calculated on a molarity basis (2.5% molarity basis = 3.3% on a weight basis) and assumes all the added AQ is converted to AHQ.
[c]Comparing this percent to the percent used in pulping is difficult since (1) vanillyl alcohol has a lower molecular weight than the typical lignin monomer (138 to 172), (2) wood is only 25% lignin, (3) not all the lignin units in wood are capable of forming QMs, (4) most of the lignin units in wood that form QMs also further react by β-aryl ether cleavage and (5) vanillyl alcohol can only undergo condensation reactions.
[d]The analyses were single determinations. The precision is not known, but is estimated to be ± 0.2-0.3. The numbers listed correspond the GC signal area relative to a benzil internal standard (equated to 1.0).
[e]No glucose was present in this control run.

is "what species is present to complete the redox cycle"? Glucose is known to be rapidly consumed by warm alkali.[12] Possibly, the VA-AHQ reactions are very rapid and are, thus, able to benefit from unreacted glucose. Maybe glucose by-products play a role.

Several other VA condensation reactions were run in which an additive other than AQ or AHQ was used. For example, VA was heated with alkali and sodium sulfide. Analysis of the resulting products by GC showed, in comparison to a control cook, somewhat reduced levels of dimers but higher levels of trimer. Under the same conditions, AHQ showed a large reduction in dimer and trimer

levels. Thus, it appears that sodium sulfide, a delignification aid present in the kraft pulping process, is not very effective at retarding VA condensation reactions. [The pH was 13.0-13.7 during the reactions; therefore, the sulfur may be present as a mixture of S^{-2} and SH^-.]

In contrast, sodium dithionite was an excellent additive for retarding VA condensation reactions. Dithionite was examined as an additive for possible use in the VA/AQ cooks for generating AHQ *in situ*. Another compound which depressed VA condensation reactions is 3,5-dinitrobenzoic acid (DNBA). This compound was chosen for examination because of the likelihood that it would suppress radical anion reactions.[21] The data in Table 2 show the analysis of some vanillyl alcohol cooks done at 100° with and without 0.1 equivalent of DNBA and/or AHQ. Glucose is absent in these cooked

TABLE 2

Gas Chromatographic Analysis of the Derivatized Product Mixture of Vanillyl Alcohol Cook Samples

	Relative Amount[a] for Various Cooks[b]			
Component	—	AHQ[c]	DNBA[c]	AHQ/DNBA[c]
Monomers	4.1	3.2	2.2	6.3
Benzil	1.0	1.0	1.0	1.0
AQ	—	0.9	—	small
Dimers	13.5	4.4	6.5	3.5
Adduct	—	2.3	—	—
Trimers	4.6	2.0[d]	2.3[d]	1.1[d]
Tetramers	5.5	0.1	—	—

[a]Quantities present relative to benzil internal standard assuming a 1:1 GC response factor.

[b]Cooks were done at 100°C, in glassware, under nitrogen, for 2 hours. At the conclusion, the samples were exposed to air, filtered to remove most of the AQ, and acidified to obtain the product. The product mixture was dissolved in THF and derivatized with Me_2SO_4/OH^- prior to GC analysis.

[c]The additive level was 0.1 equivalent relative to VA; AHQ was generated by the dithionite method and the excess dithionite removed.

[d]The retention time of this component differed from the control and, thus, may correspond to something other than a trimer.

samples; the true effects of the additives, acting alone, are thus apparent. The analysis conditions employed in this set of experiments were modified in order to observe the production of tetramers.

What properties do AHQ, dithionite and DNBA have in common that make them good inhibitors of vanillyl alcohol condensation reactions? Dithionite is a good electron donor; it is used in alkaline solution to convert AQ to AHQ^{-2}. The addition of 3,5-dinitrobenzoic acid to an alkaline solution of anthrahydroquinone dianion leads to a rapid discharge of the red color associated with AHQ^{-2} and the formation of AQ. Therefore, AHQ^{-2} is an electron donor relative to DNBA. Perhaps all three of these additives function as electron donors to, let's say, a quinonemethide, converting the latter to a form that does not readily undergo condensation reactions. Significant quantities of vanillin and aldehydic compounds were observed in the DNBA cook product mixture; perhaps DNBA is functioning strictly as an oxidation catalyst.

A comparison was made of the product compositions of vanillyl alcohol cooks done in the presence of glucose and glucose/AQ (AHQ) at temperatures ranging from 85-173°. The trimer level in the glucose set increased by a factor of 50 over this temperature range, while the level of trimer was nearly constant in the glucose/AQ set. At 85° (Fig. 3), the trimer level was actually higher in the glucose/AQ run; the dimer levels were nearly identical. This trend was reversed at 115° and above. The distribution of dimer components also changed with temperature; dimer 9 was more abundant at the lower temperatures.

The level of adduct in the glucose/AQ product mixtures decreased as the temperature of the cooks increased. The adduct is known to dissociate in aqueous alkali at temperatures above 60° to AHQ and a quinonemethide.[21] Under conditions where adduct stability should be the highest (85°), condensation product levels were also high, relative to the control. Therefore, lowering the relative concentration of quinonemethide 3 through adduct formation appears to have little influence on the degree of condensation reactions.

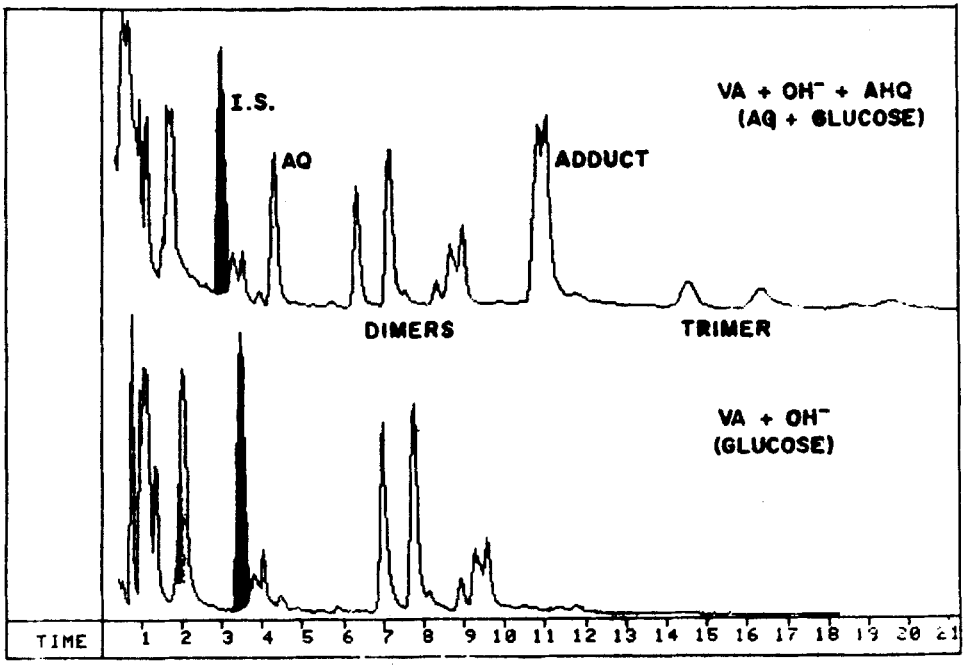

Figure 3. Comparison of the Gas Chromatograms of the Derivatized Products Obtained from Vanillyl Alcohol Cooks, with and without AHQ, at a Reaction Temperature of 85° for 2 Hours. The Retention Times Differ Slightly Due to Slightly Different Chromatographic Conditions

The level of dimers and trimers in both the glucose and glucose/AQ runs done at low temperature (135° or less) were only about 1% or less. For 100° cooks containing no glucose the yields were an order of magnitude higher (Table 2). Apparently, glucose has a substantial inhibiting effect at low temperatures, where its lifetime in alkali is longer.

Condensation Reactions of Dioxane Lignin

Loblolly pine dioxane lignin of weight average molecular weight of approximately 11,000[22] was heated with aqueous alkali, with and without additives present. The additives examined were AQ (10% by weight, relative to the dioxane lignin), glucose (100%

by weight) and a glucose-AQ combination. After heating (173°) for 45 minutes, the reaction mixtures were cooled, acidified and freeze-dried. The molecular weight profiles of the dioxane lignin and the various products were compared by gel permeation chromatography using a SynChropak GPC 100 column and dimethylsulfoxide (DMSO) as the solvent, Fig. 4. The molecular weight profile of

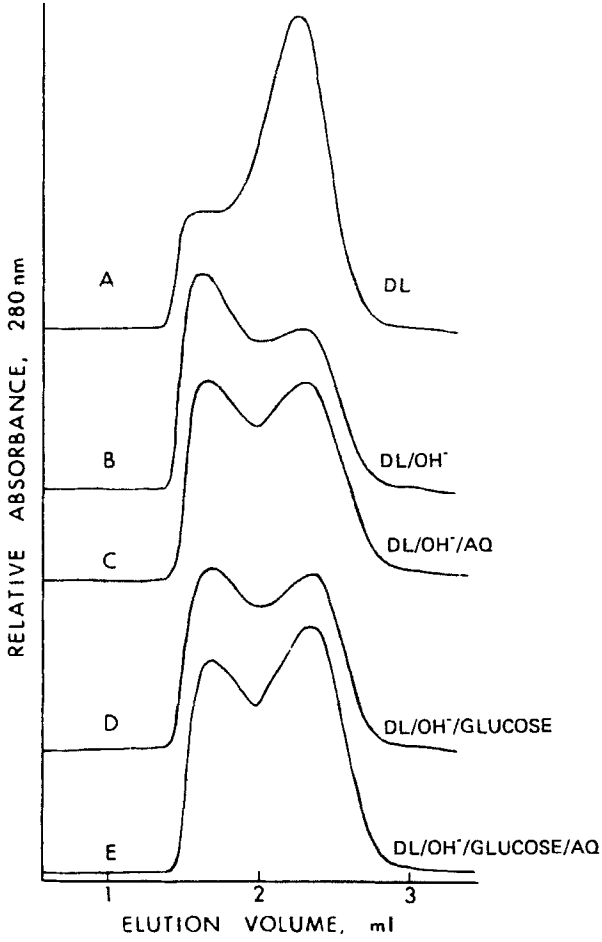

Figure 4. Gel Permeation Chromatograms of Dioxane Lignin (DL) and its Reaction Products with Alkali and Some Additives

the dioxane lignin by this method was in excellent agreement with the profile obtained by gel filtration through a Sephadex G-100 column.[22]

All of the cooks produced lignin of higher molecular weight than the starting dioxane lignin; however, the cooks containing additives (Fig. 4, C-E) gave less higher molecular weight material than the control (Fig. 4, B). The cook containing AHQ gave the least amount of higher molecular weight condensation products. The effects of AHQ might have been more pronounced if we had designated the experiment to provide a continuous means of regenerating AHQ. The results shown in Fig. 4 qualitatively agree with the results of several other lignin/AHQ molecular weight studies.[7,23-25]

Perhaps a note of caution should be added at this point concerning GPC data on lignin. Lignin can adhere strongly to column packings unless a very polar solvent is employed. Most GPC columns do not perform well when polar solvents are used. The main application area of the SynChropak column used in our studies has been in the analysis of proteins[26] and carbohydrates.[27] The column adsorbed some lignin, giving distorted shapes, when 20% aqueous dioxane was used as the solvent, but *appeared* to function well with DMSO as the solvent.

Besides adsorption effects, GPC molecular weight profiles can be distorted by changes in chromophores when using an ultraviolet (UV) detection system. An additive, like AQ, could cause additional chromophores *via* oxidation reactions[28] which may not be uniform across all molecular weight components.

A third problem with GPC is that unwanted UV absorbing species can interfere with the analysis. In manipulating to remove AQ, a strong UV absorbing low molecular weight material, one might change the sample's composition by selectively removing both high and low molecular weight lignin during acidifications and filtrations. There is evidence that AQ becomes bound to the alkali soluble lignin found in soda/AQ pulping liquors.[29] This could affect the UV absorbance of specific lignin molecular weight ranges.

CONCLUSIONS

The condensation reactions of vanillyl alcohol are sensitive to reaction temperature and additives, such as AHQ, dithionite, 3,5-dinitrobenzoic acid and glucose. The reactions appear to be relatively insensitive to sulfide ion, AQ and QM-AHQ adduct levels.

The most satisfying way to demonstrate differences in condensation levels is by observing differences in molecular weight changes. Due to technical problems, we were unable to determine (by GPC) the molecular weight distribution of the *whole* sample after a vanillyl alcohol condensation reaction. The GPC-determined molecular weight distributions of condensed dioxane lignin samples suggested that AHQ inhibited condensation reactions in this system; however, the method of analysis has several drawbacks which could affect the conclusions drawn.

In a polymerization reaction, the level of monomer will steadily decrease with time. The levels of dimers, trimers, etc., will at first grow and then later drop off in favor of the next larger oligomer. After 2 hours reaction time, a distribution of polymerized materials developed from the reaction of vanillyl alcohol with alkali. Derivatization and GC/MS analysis of the product only showed monomer-tetramer materials. The yields of these were rather low (~ 20%) presumably because the bulk of the material was polymerized to a higher level. The ratio of monomer:dimer:trimer:tetramer, assuming equal GC response factors, was roughly 1:3:1:1.2 (Table 2).

An identical alkaline reaction of vanillyl alcohol, except done in the presence of AHQ, had a yield of monomer similar to the control but only about 1/3 the level of dimer and practically no tetramer. This distribution of products, even though low in relative yield, does not fit a polymerization process. The question is: "What alternative process occurs in the presence of AHQ"? The only new product observed in this system was an AHQ adduct of vanillyl alcohol and its yield was low.

The NMR analyses of the ether soluble portion of vanillyl alcohol reaction mixtures confirmed the presence of condensed materials and showed major differences for the control and AQ runs *vs.* the AHQ run. This analysis technique may also be restricted to observing low molecular weight polymeric material, since the higher molecular weight fraction may not be ether soluble. Consequently, the bulk of our conclusions rests on analyses of lower molecular weight products and infers that high molecular weight materials exist, at least in the control runs.

Thus, while we showed that a major difference occurs in vanillyl alcohol condensations in the presence of AHQ, we do not have an adequate explanation as to what new chemistry is involved.

Before fully understanding the role of additives on condensation reactions, it may be necessary to reexamine the mechanism of these reactions. The ionic pathways presented in Fig. 2 may or may not best explain how vanillyl alcohol condensation products arise. To what extent are radical mechanisms important? Why do additives which are good electron donors or acceptors seem to inhibit this process?

It would appear that the rapid delignification rates which accompany pulping with AQ can be explained by a combination of AHQ acting to promote lignin fragmentation reactions and to retard lignin condensation reactions.

EXPERIMENTAL

Proton NMR spectra were recorded on Jeol FX 100 spectrometer using $CDCl_3$ as the solvent and TMS as an internal reference. The GPC analyses were performed with a Varian 8500 pump and Perkin-Elmer LC-55 UV detector. Infrared spectra were recorded on a Perkin-Elmer Model 700 Infrared Spectrometer and standardized with polystyrene. The preparative gas chromatography employed an Aerograph 200 GC with a thermal conductivity detector and a 6' x 1/4" column of 5% SE-30 on 60/80 chromosorb W column.

Gas chromatographic analyses of derivatized samples were done either on a Perkin-Elmer 3920 GC, using a 6' SE-30 (3%) on

Chromsorb-W column and nitrogen carrier gas flow of 30 mL/minute, with temperature programming of 120° to 250° at 8°/minute and detection by flame ionization (Fig. 1) or a Hewlett Packard 5840 GC, using a 2' OV 101 (2%) on Ultrabond 20M column, with temperature programming of 150° to 225° at 10°/minute and detection by a Hewlett-Packard 5985 mass spectrometer (Fig. 3). The all glass GC/MS system employed helium (30 mL/minute) as the carrier gas, a jet separator at 250°, a source temperature of 200° and an ionization voltage of 70 eV when operated in the electron impact (EI) mode. Methane (30 mL/minute) was used as the carrier gas with a direct line to the source (200°), operating at 230 eV, when obtaining chemical ionization (CI) spectra.

Vanillyl Alcohol Control Cook. - Into a 50 mL titanium pressure vessel was added 154 mg (1 mmole) of vanillyl alcohol and 30 mL of 0.5N NaOH. The vessel was purged with nitrogen, sealed and rotated in a preheated oil bath at 173° for 2 hours. The vessel was quickly cooled to room temperature, opened and the contents stirred in air for a few minutes and then acidified to pH 6-7 with concentrated HCl to afford a precipitate. The water was next removed by either freeze-drying or extracting with ether; the ether extract was dried (Na_2SO_4) and evaporated in air at room temperature. [When working-up an additive run, the air exposure converts AHQ^{-2} to AQ, which is incorporated into the freeze-dried residues or filtered away before acidification in the ether extraction procedure.]

Several freeze-dried VA cook samples, with and without AQ, were extracted with saturated sodium bicarbonate solution. The bicarbonate soluble portion was acidified with concentrated HCl, then extracted with ether. The ether extract was dried over anhydrous Na_2SO_4 and the solvent removed on a rotary evaporator. The residue was analyzed by IR and the spectrum compared to that of vanillic acid. No evidence for vanillic acid in cook samples was found based on the complete absence of an absorption at 750 cm^{-1} in the IR spectra of these residues.

Positive identification of several components of the VA cook samples was achieved by methylating[30] known or synthesized com-

pounds and comparing GC retention times and mass spectra. These compounds included vanillyl alcohol (1), vanillin (5), bis-(3-methoxy-4-hydroxyphenyl)methane (7), 1,2-di-(3'-methoxy-4'-hydroxyphenyl) ethane (13) and 10-methoxy-10-(3'-methoxy-4'-hydroxybenzyl)-9(10H)-anthracenone (14).[31] The latter component was only observed during the VA/AHQ cooks. Two compounds were identified based on comparison to the data of Yoon[18] and Hemingson,[19] NMR spectra of GC collected samples and the mass spectral fragmentation patterns;[15] these were 3-(3'-methoxy-4'-hydroxybenzyl)-4-hydroxy-5-methoxybenzyl alcohol (9) and 1,2-di-(3'-methoxy-4'hydroxybenzyl)-6-methoxyphenol. Many of the lesser components of the product mixtures have been tentatively identified by means of EI and CI mass spectra.[15] Duplicate cooks performed simultaneously gave nearly identical product distributions.

A few of the ether extracted cook samples were analyzed by GC before derivatization and retention times compared to that of authentic creosol (4); no significant level of creosol was observed.

Severe tailing and irreproducible results were observed when precipitated product samples were dissolved in 25% aqueous dioxane and analyzed by GPC using μ-Bondagel or μ-Bondagel/μ-Porasil columns. Direct analysis of alkaline product mixtures gave similar results.

Vanillyl Alcohol Cooks with Additives. Standard VA cooks as described above were done in the presence of various additives. The additives included AQ (208 mg, 1 molar equivalent), or glucose (540 mg, 3 molar equivalents), or a combination of the two additives. One set of cooks was done with varying levels of AQ; the conditions and relative amounts are detailed in Table 1. In another set of cooks varying levels of sodium dithionite ($Na_2S_2O_4$, 90%, technical grade) were added to the standard VA cooks with and without AQ (208 mg, 1 molar equivalent) present. Dithionite levels were 47.9 mg of 90% pure material (0.25 molar equivalent), 95.9 mg (0.50 molar equivalent) and 191.8 mg (1.0 molar equivalent).

A set of additive cooks, including 3,5-dinitrobenzoic acid (DNBA), were done at 100° in glassware. The conditions are detailed in Table 2. The AHQ^{-2} was generated by a dithionite method,[31] rather than with glucose.

A series of cooks was done at various temperatures. At each temperature, a control sample (154 mg VA and 540 mg glucose in 30 mL of 0.5N NaOH) and an AQ sample (154 mg VA, 540 mg glucose and 208 mg AQ in 30 mL of 0.5N NaOH) were cooked 2 hours in a titanium bomb. The four temperatures were 85°C, 115°C, 135°C, and 175°C. Samples were worked up by the freeze-dry method and analyzed by GC, after methylation.

1,2-(3',4'-Dimethoxyphenyl)ethane (13). - The synthesis of this compound depended upon the fact that dibenzyl compounds are a common by-product when benzyl Grignard reagents are made.[32] An ether solution of 10 g (53.6 mmoles) of 3,4-dimethoxybenzyl chloride[33] was slowly added to a stirred suspension of 0.65 g (26.7 mg-atoms) of magnesium turnings in anhydrous ether. The reaction was very difficult to initiate. The reaction mixture was stirred at reflux temperature for 3.5 hours. Much of the magnesium remained unreacted. Carbon dioxide was bubbled through the solution and the mixture allowed to stand overnight at room temperature. The ether solution was decanted from the unreacted magnesium and washed successively with dilute HCl and water, dried over anhydrous sodium sulfate (Na_2SO_4) and the ether removed on a rotary evaporator. The residue (5.8 g) was an amber, viscous liquid. Analysis of the residue by GC/MS indicated several components, one of which exhibited a strong 302 signal, corresponding to the molecular weight of coupling product 12. This component was approximately 18% of the mixture, and was the major product. Residual starting material comprised 46% of the mixture.

Bis-(3-methoxy-4-hydroxyphenyl)methane (7). - This compound was prepared according to the method of Lindgren[34] and had a mp of 99-102°C (lit. mp 101-104°C). The purified compound was derivatized by methylation with dimethyl sulfate and the derivative analyzed by GC/MS and NMR: ^{1}H-NMR ($CHCl_3$), 3.33 (s,2,CH_2), 3.84

(s,12,OCH_3) and 6.8 (m,6,aryl); ^{13}C-NMR ($CHCl_3$) PPM 41.0 (CH_2), 56.0 and 56.2 (OCH_3), 111.4 (C-2), 112.4 (C-5), 120.8 (C-6), 134.4 (C-1), 148.0 (C-4) and 149.6 (C-3); MS (70 eV) m/e (%) EI 288(100), 257(6) and 151(11) and CI 317(12), M + 29, 289(79), M + 1, 288(10), M, 287(5), M - 1, 151(100).

Dioxane Lignin Cooks. - A sample of 0.25 g of dioxane lignin, isolated by Crozier[22] and having a weight average molecular weight of 11,000, was combined with 0.2 g of NaOH and 50 mL of distilled water in a 150 mL Teflon-lined brass reactor,[22] equipped with an internal thermocouple, sample line, venting line and magnetic stirrer. The reactor was sealed, attached to a magnetic stirring device and lowered into an oil bath preheated to 173°. The reactor was vented when the temperature of the solution reached 105° (~ 15 minutes). The reaction mixture took approximately 30 minutes to reach 173°. Exactly 75 minutes from the immersion in the oil bath, the reactor was removed from the bath and plunged into cold water. The contents were removed and the pH (>12) was adjusted to 6 by the addition of HCl. The resulting mixture was freeze dried to remove moisture and stored in a desiccator.

Identical runs were performed using (1) 0.25 g of glucose, (2) 0.025 g of AQ and (3) a combination of these two.

Prior to analysis, the sample was dissolved in 1N NaOH and filtered. Analysis of the collected precipitate (in the AQ runs) by GC-MS showed it to be AQ. The filtrate was neutralized and freeze-dried. Analysis of the freeze-dried residues by UV showed no AQ signals. The samples, however, contained a large amount of salt - from two neutralizations - and displayed a third peak as a tail in the low molecular weight region of the GPC. [Tailing could be induced into dioxane lignin chromatograms by just adding salt to the sample.]

The salt was removed by dissolving the samples in water and centrifuging. The residues and supernates were each freeze-dried. Weighed centrifuged residues (0.01 g) were dissolved in 10 mL of purified DMSO and filtered through a Millipore glass fiber prefilter and a 5 µm organic filter. A 50 µL injection of the solu-

tion was eluted with DMSO through a 25 cm, 4.1 mm inside diameter, SynChropak GPC 100 column at a rate of 15 mL/hour. The eluant was analyzed by a UV detector at 280 nm. The results are given in Fig. 4.

Analysis of supernatant liquid freeze-dried residues showed a low concentration of low molecular weight material which was similar from one run to the next.

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